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INTERRUPTED STRESS-STRAIN EXPERIMENTS WITH NYLON 6

JEROME RUBIN

MARCH 1972

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Samples of nylon 6 were subjected to drawing from a few percent to greater than a hundred percent and allowed to stress relax. This involved elongating the sample to a certain point and then keeping the length constant. When the sample is momentarily held at the peak of the original yield point and then pulled again, a higher-than-original yield peak develops. Subsequent interruptions followed by drawing resulted in the formation of additional yield peaks. In each of these latter cases, the new yield peak is lower than the original. It has been found that any number of yield peaks can be formed as long as any undrawn material still remains and/or as long as the sample is allowed to stress relax. The height of the new yield peak formed is related to the time allowed for stress relaxation. Simple unloading of the sample does not cause the same effect. It is shown that the stress relaxation plays an integral role in the structural rearrangements which lead to the development of additional yield peaks.

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Interruption of curves						
Relaxation of stress						
- at yield point of curve						
- in cold drawing region						
- in linear portion						
Duration of period of relaxation						
Complete unloading of specimen						
Instron testing machine						
Reversibility of yielding process						
Structural breakdown (possible molecular) during necking						
Polyamide						

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OBJECT

To study the mechanical response of nylon during interrupted stress-strain experiments on the Instron.

SUMMARY

Samples of nylon 6 were subjected to drawing from a few percent to greater than a hundred percent and allowed to stress relax. This involved elongating the sample to a certain point and then keeping the length constant. When the sample is momentarily held at the peak of the original yield point and then pulled again, a higher-than-original yield peak develops. Subsequent interruptions followed by drawing resulted in the formation of additional yield peaks. In each of these latter cases, the new yield peak is lower than the original. It has been found that any number of yield peaks can be formed as long as any undrawn material still remains and/or as long as the sample is allowed to stress relax. The height of the new yield peak formed is related to the time allowed for stress relaxation. Simple unloading of the sample does not cause the same effect. It is shown that the stress relaxation plays an integral role in the structural rearrangements which lead to the development of additional yield peaks.

INTRODUCTION

Studies of the mechanical properties of polymers have long been used to determine the physical limitations of the material for use in writing specifications. More recently however, mechanical properties studies have been found to be useful in helping to elucidate the structure of the material (Ref 1, 2, 3, 4). The techniques usually employed involve the Instron testing machine and creep experiments conducted either together or separately. A newer technique for dynamic mechanical testing makes use of the Rheovibron Tensiometer. This instrument can be used to determine transitions in the polymer such as the glass transition and low temperature molecular motion (Ref 5). In this study, however, the work was concerned with the stress-strain curve as obtained on the Instron.

Many studies of mechanical properties of polymers have been made on the Instron. Carswell and Nason (Ref 6) have divided the types of stress-strain curves obtained with polymers into five classes: (1) soft, weak; (2) hard, brittle; (3) soft, tough; (4) hard, strong; (5) hard, tough. The polymer under study here, nylon 6, falls into the class of hard, tough polymers. It has a well-defined yield point, undergoes cold-drawing, and has high tensile strength. In this study we were not especially interested in the stress-strain curve per se, but in the "yield" phenomenon. Vincent (Ref 7) had shown that if the stress-strain curve is interrupted in the cold-drawing region, a new yield peak will form in one case but not another. The aspect emphasized here was the effects of interrupting the stress-strain tests. In some cases, the experiment was stopped at the yield peak and allowed to stress relax. This was also done in other parts of the stress-strain curve. In other tests, the sample was unloaded completely and then pulled again. This type of investigation has not been done previously on nylon 6.

EXPERIMENTAL PROCEDURES

The material was Allied Chemical Company's caprolactam nylon 6 film, 1 mil in thickness. The sample size was 1 inch wide and 2 inches between clamps. All testing was done on a standard Instron testing machine. The crosshead and chart speeds were both 2 inches/min giving a strain rate of 100%/min. The stress relaxation was done by elongating the sample to the length desired and then stopping the

downward travel of the crossbar. The unloading experiments were done by reversing the downward travel of the crossbar without stopping at all. The film was not treated in any way prior to use; therefore, it contained an equilibrium amount of moisture. Moreover, the room was thermostated at 72° F and 50% R.H., so all testing was done at constant temperature and humidity.

RESULTS

The original stress-strain curve of nylon 6 is that of a typically cold-drawing material (Fig 1). There is a well-defined yield point followed by the relatively constant-stress region during which the sample is necking down. After all the material between the clamps has necked down, there is a sharp, almost linear, rise up to the breaking point. With minor variations, this is the type of curve one obtains from an uninterrupted tensile experiment on the Instron testing machine. However, when the experiment is interrupted, major variations occur, the nature of which depends on the point at which the experiment is stopped.

In Figure 2, the sample was elongated up to the yield point and then held constant. The sample "stress relaxes" spontaneously, very sharply at first then much more gradually as an asymtotic function would. When the sample was elongated again, the yield peak that formed was higher than the original. Even the shape was different. There was a pointed peak superimposed on the original shape. The rest of the stress-strain curve followed the usual pattern. There was a cold-drawing region followed by the upward turn to the breaking point.

Figure 3 shows a sample that was handled only slightly differently. The sample was elongated up to the yield peak and then stopped, allowed to stress-relax, and pulled again. As before, the yield peak is higher than it otherwise would have been. In the middle of the cold-drawing region, the elongation was again held constant. Once more the sample stress relaxed. When the sample was elongated again, another yield peak formed, lower than the first but above the cold-drawing region. The elongation was also stopped and allowed to stress relax toward the end and pulled again. Even in this region, another yield peak developed. After this yielding, the stress level rose sharply to the ultimate extension.

This series shows that not only can a higher-than-original yield peak be formed, but also yield peaks can be developed in the cold-drawing region and in the upper portion of the stress-strain curve as well. These phenomena have not been shown before.

Another sample was allowed to stress relax three times in the cold-drawing region, as can be seen in Figure 4. Each time the experiment was continued a new yield peak developed. It was always smaller than the original but clearly defined above the normal cold-drawing stress level. More yield peaks were observed in the upper portion of the stress-strain curve as well. It seems there is no limit to the number of yield peaks that can be developed in any portion of the curve. The yielding behavior of nylon is obviously not a one-time event, but can be generated as often as desired provided there is still undrawn material left in the sample and it has been allowed to stress relax.

All the samples up to this point had been allowed to stress relax at the peak of the yield point. Figure 5 shows the results of allowing the sample to form the initial yield peak first and then interrupting the experiment in the cold-drawing region. The sample was allowed to stress-relax four times in the cold-drawing region and each time a new yield peak formed when the sample was pulled again. The yield peaks were also formed in the upper portion of the curve.

This shows that the sample can be pulled in the usual fashion to form the normal yield peak and still any number of yield peaks can be formed again. It is true, however, that each of the successive yield peaks formed is always much smaller than either the original normal one or the new one formed by stress relaxing at the original yield point. In Figure 6, we see a sample that has nine yield peaks after the original, all of which are within the cold-drawing region.

A slight variation was made in the testing procedures used to obtain the results reported in Figure 7. The sample was allowed to form the original yield peak and then allowed to stress relax the first time at the onset of cold-drawing. This sample was allowed to stress relax for only seconds and pulled again. Each time the sample was allowed to relax for only a few seconds right after the yield peak formed. First, it can be seen that there are many yield peaks in what would normally be the cold-drawing region. Also, the new yield peaks are much shorter than those formed in the other experiments. This

means that the height of the new yield peaks is also related to a certain extent to the time allowed for stress relaxation. It may very well be that the longer the sample is allowed to stress relax the higher the new yield peak will be.

Some evidence of this is offered in Figure 8. The sample was allowed to stress relax first at the maximum of the original yield peak with the expected result that the new yield peak formed is higher than it would have been otherwise. The sample was then allowed to stress relax for longer time periods. It can be seen that these yield peaks are much higher than those obtained in the previous case in which the sample was allowed to stress relax for only a very short time.

These results permit one to draw certain conclusions concerning the cold-drawing of nylon:

1. The "yielding" of the sample does not necessarily have to be limited to a single occurrence. It is limited to a single event if the sample is pulled continuously without interruption.

2. Allowing the sample to stress relax at the maximum of the original yield point will produce a new yield peak that is of greater intensity than the original.

3. Yield peaks can be formed in the cold-drawing region as well as in the final portions of the stress-strain curve

4. The longer the sample is allowed to stress relax the higher the new yield peak will be, within certain limits.

Some interpretation of what is transpiring at the molecular level is also possible at this time. The initial yielding of the polymer involves a breakdown of structure of some kind. It is not known, though, whether it is really at the molecular level or of a higher, gross structure sort. However, one thing is clear. The breakdown is neither permanent nor completely irreversible. Part of the original structure can be recovered through the stress relaxation process. The only condition under which the breakdown gives the impression of being complete or permanent is if the sample is pulled continuously. And here it is misleading because of the stress concentration in the necking zone which causes the neck to propagate. It is clear that,

if for some reason the original neck did not propagate once formed, a new yield peak would develop along with a new necking region. This must mean that the structural breakdown is actually going on during the cold-drawing stage at the shoulder of the neck.

The ability of the sample to undergo stress relaxation means that there is continued molecular motion in the original pull direction even though the sample is not being elongated at this time. This continued orientation has the effect of elongating the sample which reduces the stress level originally imposed. This effect is somewhat similar to the Le Chatelier principle which accounts for the changes in equilibrium concentrations when an external force is applied. The analogy should not be carried too far, however, as the system under discussion here involves physical changes of state as opposed to reversible chemical reactions.

Evidence for the somewhat reversibility of the yielding process comes from the experiments in which the sample was elongated up to the yield peak and then held at constant length. After the sample was allowed to stress relax at the maximum of the yield peak and pulled again, it was found that the new yield peak was much higher than the original would have been. This combination of events seems to represent a contradiction in what is occurring. First of all, for the sample to stress relax means the sample must continue to orient itself in its direction of pull to relieve the stress. Logically then, it would seem reasonable for the original structure to be breaking down more. However, to obtain a higher-than-original yield peak, it would seem to be a prerequisite for the sample to be capable of returning to its original structure in a more stable or lower energy state. If the new state after stress relaxation were not more rigid, how could one account for the higher yield peak?

It is conceivable, however, that pulling the sample up to the top of the original yield peak and holding it there does not completely break down the original "set", but imparts mobility to it. Now, even though the sample is stress relaxing, which means the structure is rearranging to relieve the stress, the structure being formed during this stress relaxation period must be more rigid than the original. It is also possible that analysis at this point would not show a great deal of molecular motion, but perhaps a very small amount of chain mobility coupled with "domain" or section mobility.

It has also been found that merely interrupting the stress-strain experiment is not sufficient to render these phenomena observable. The sample must be allowed to stress relax at the original yield peak to achieve the higher new yield peak. If the sample is not allowed to stress relax, this effect is not observed.

The importance of the role of stress relaxation in forming new yield peaks is clearly demonstrated in Figure 9. In this case, the sample was not allowed to stress relax at all, but was simply unloaded quickly and completely. The sample was elongated initially just up to the onset of cold-drawing (at the top of the yield peak) and the stress was then quickly removed so that stress relaxation could not occur.

When the sample was pulled again, it did not reach the same stress level as it had originally. It was unloaded at its peak stress level as the first time and pulled again. This was done several times and each time the peak stress level was found to be lower than the previous one. Finally, the peak stress level that was reached remained the same even though the sample was loaded and unloaded at short intervals. After many of these cycles, the stress level began to rise again but only briefly. The sample started to tear at this point and could not be used further.

These results clearly show the difference in the response of the material between stress relaxation cycling and unloading experiments. After stress relaxation the new yield peak formed was higher than the original stress level. In the case of unloading experiments, there is no indication of this phenomenon at all in the original yielding region.

Another interesting observation can be made from Figure 9. Even though the curves represent discontinuous phases, the outline of the result represents the actual stress-strain curve that is obtained from a continuous pull. This means that, although the sample did not give the impression of yielding and cold-drawing, this is exactly what had occurred. The sample had yielded and cold-drawn in stages rather than in a single pull.

The size of the yield peaks that do develop after unloading is hown in Figure 10. The sample was unloaded initially right after the yield point where cold-drawing begins. The first new yield peak therefore

occurred in the cold-drawing region. It can be readily seen that it is much smaller than the new yield peaks formed after stress relaxation. When this peak had developed fully, the sample was unloaded again. Another small yield peak formed when the sampe was pulled again. This was done many times with the same effect; only small yield peaks developed. There was no indication of the sharp high yield peaks that form after stress relaxation.

CONCLUSIONS

It is rather difficult to offer a definitive interpretation of what is going on during cold-drawing much less interrupted cold-drawing experiments. Although we would have liked to add to the understanding of cold-drawing, the present study must be taken more in the light of observations which, in conjunction with other observations, may lead to satisfactory explanations.

It is our intention to examine the structure of the polymer closely for distinguishing features which may have developed in the course of these experiments. In addition, other polymers will be studied to see whether what is reported here is specific in nature to nylon 6 or is rather a general tendency of polymers under stress.

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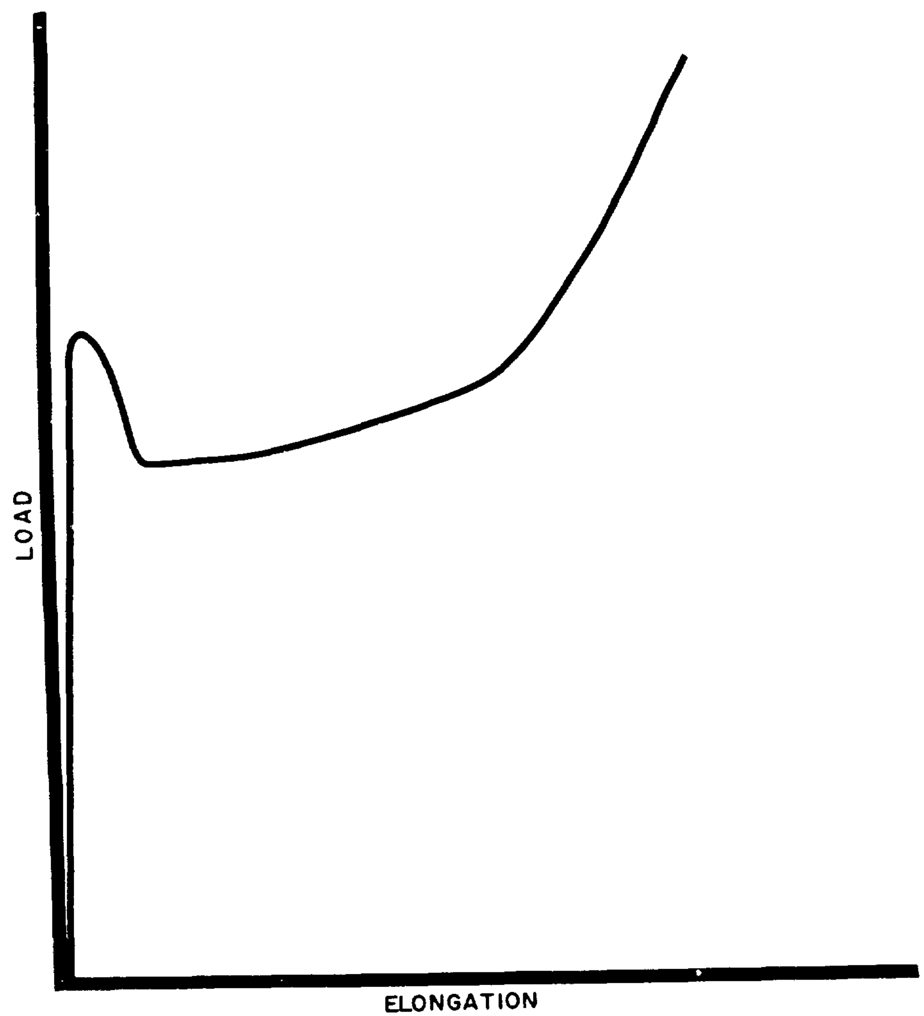

Fig 1   Stress-strain curve of nylon 6

Fig 2 Stress-strain curve interrupted at yield point; sample allowed to relax and then pulled again

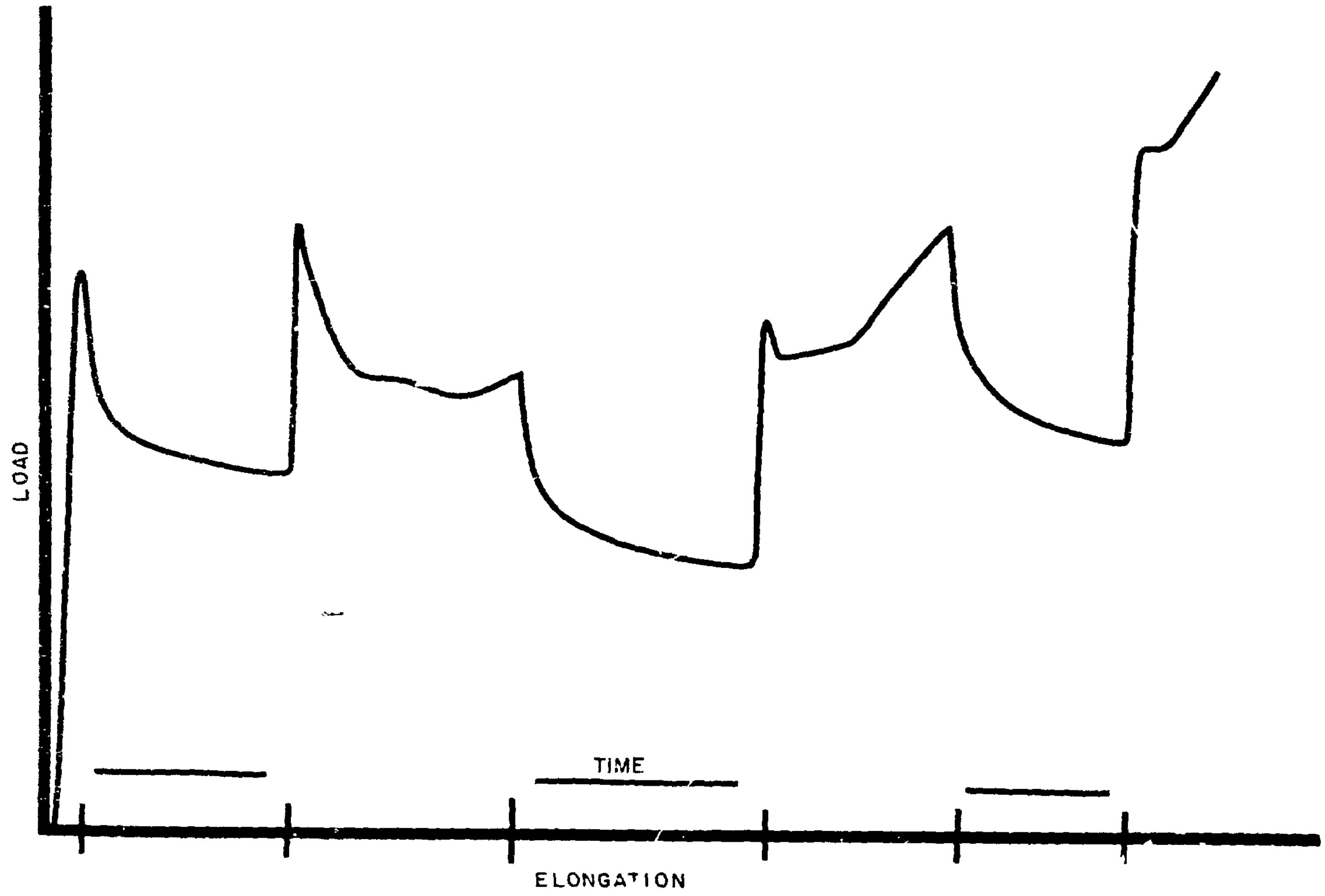

Fig 3 Stress-strain curve interrupted at yield point, in cold-drawing region, and in linear portion

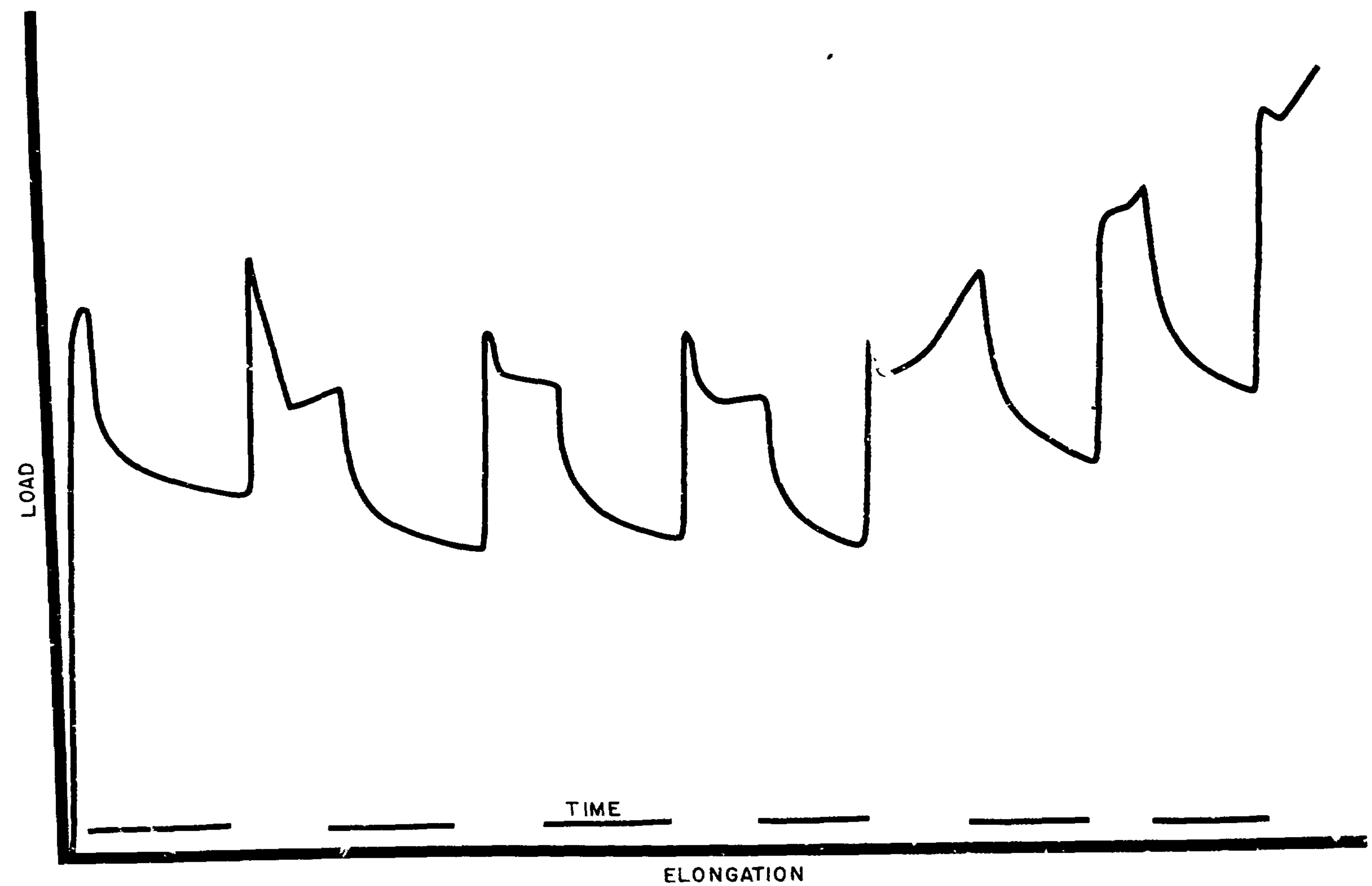

Fig 4 Stress-strain curve interrupted at yield point and at five subsequent points

Fig 5 Stress -strain curve interrupted seven times in cold-drawing region

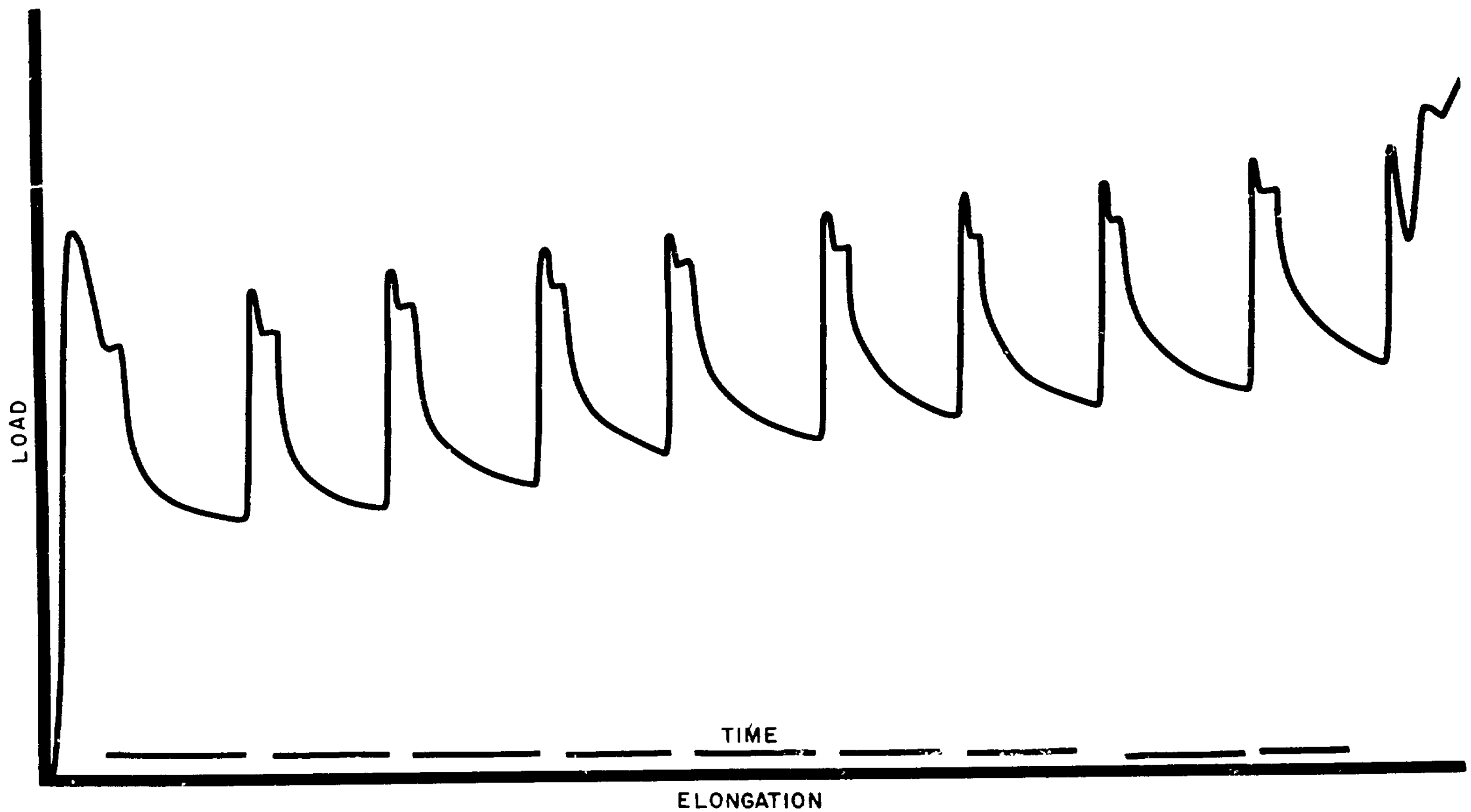

Fig 6   Stress-strain curve interrupted nine times in cold-drawing region

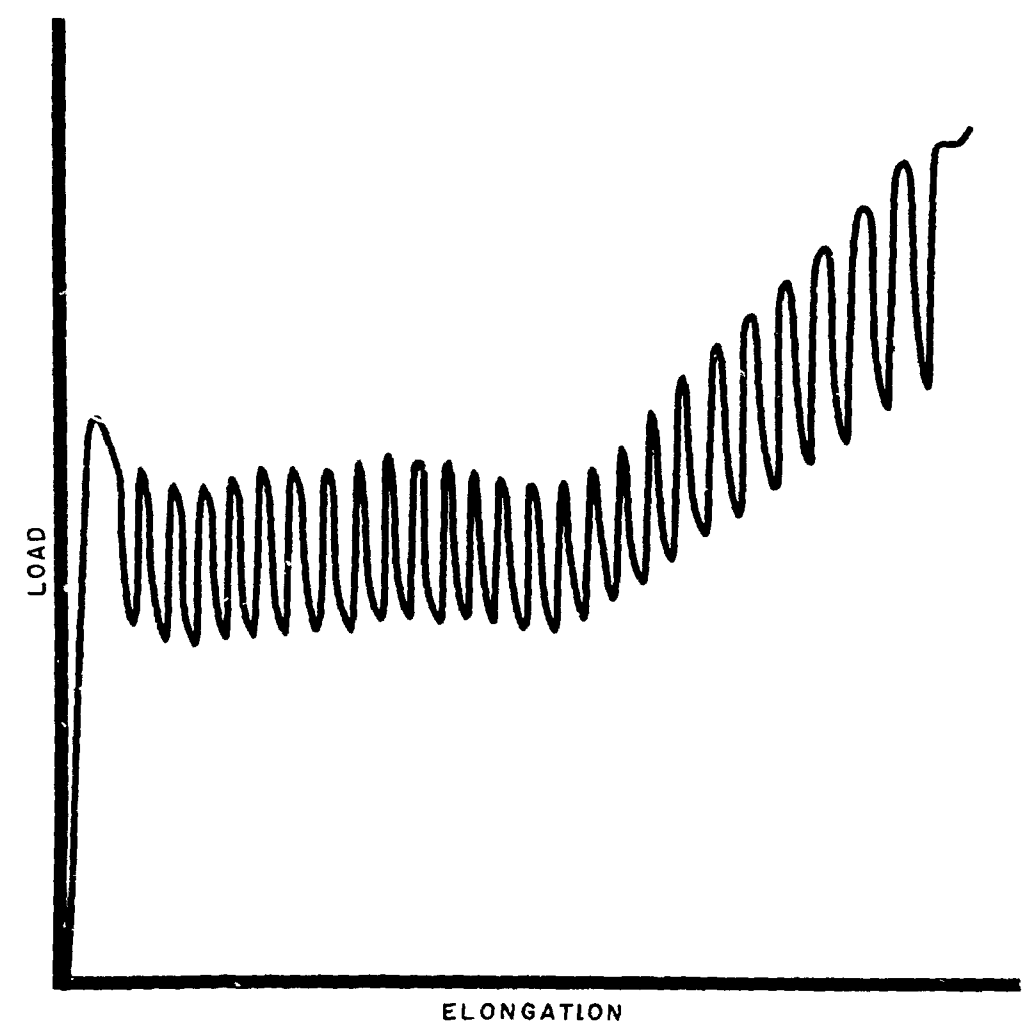

Fig 7 Stress-strain curve of sample allowed to relax for a brief period (only a few seconds) after yield peak formation

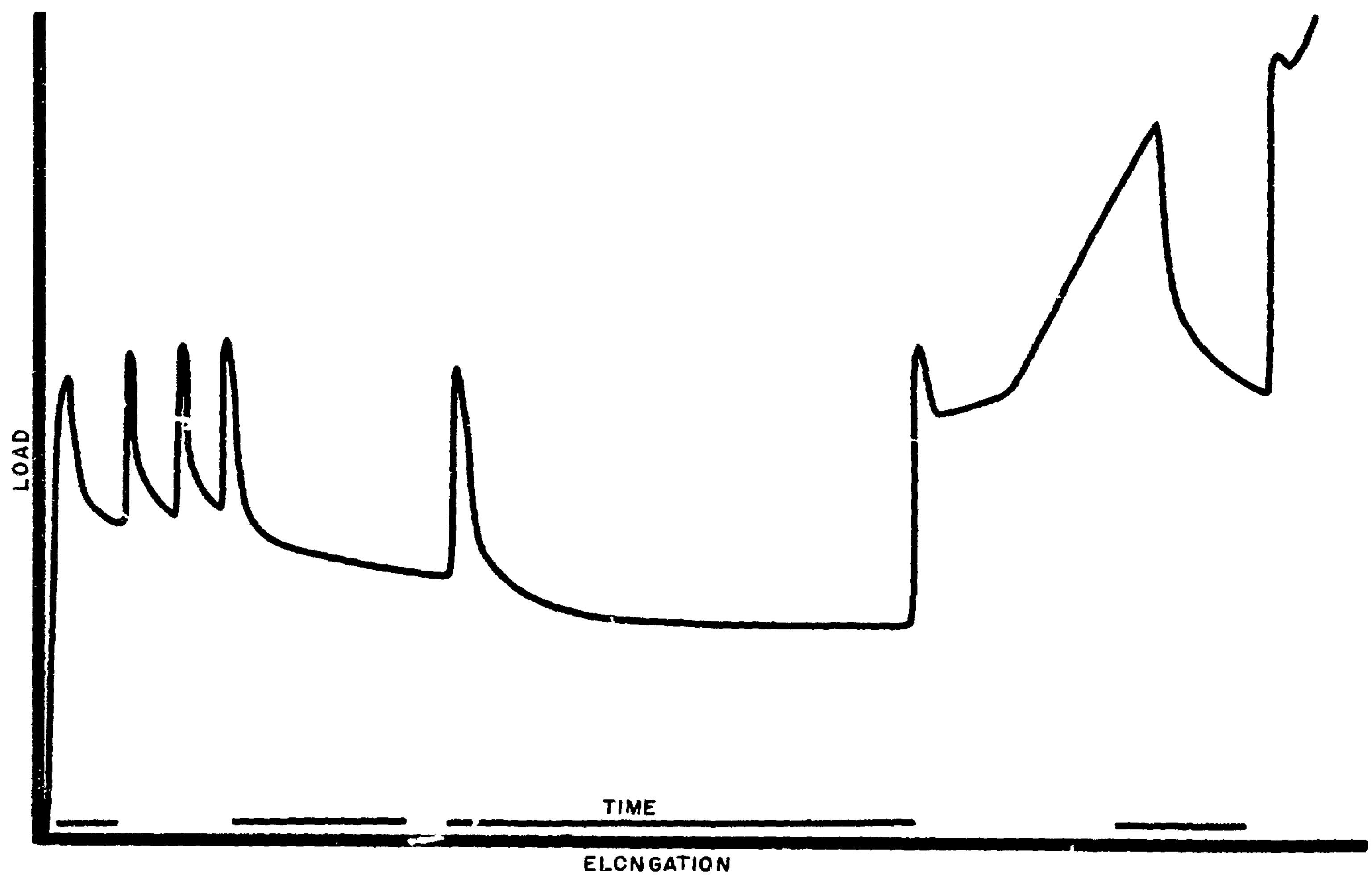

Fig 8 Stress-strain curve of sample allowed to relax, first briefly after yield peak formation and then after several longer time periods

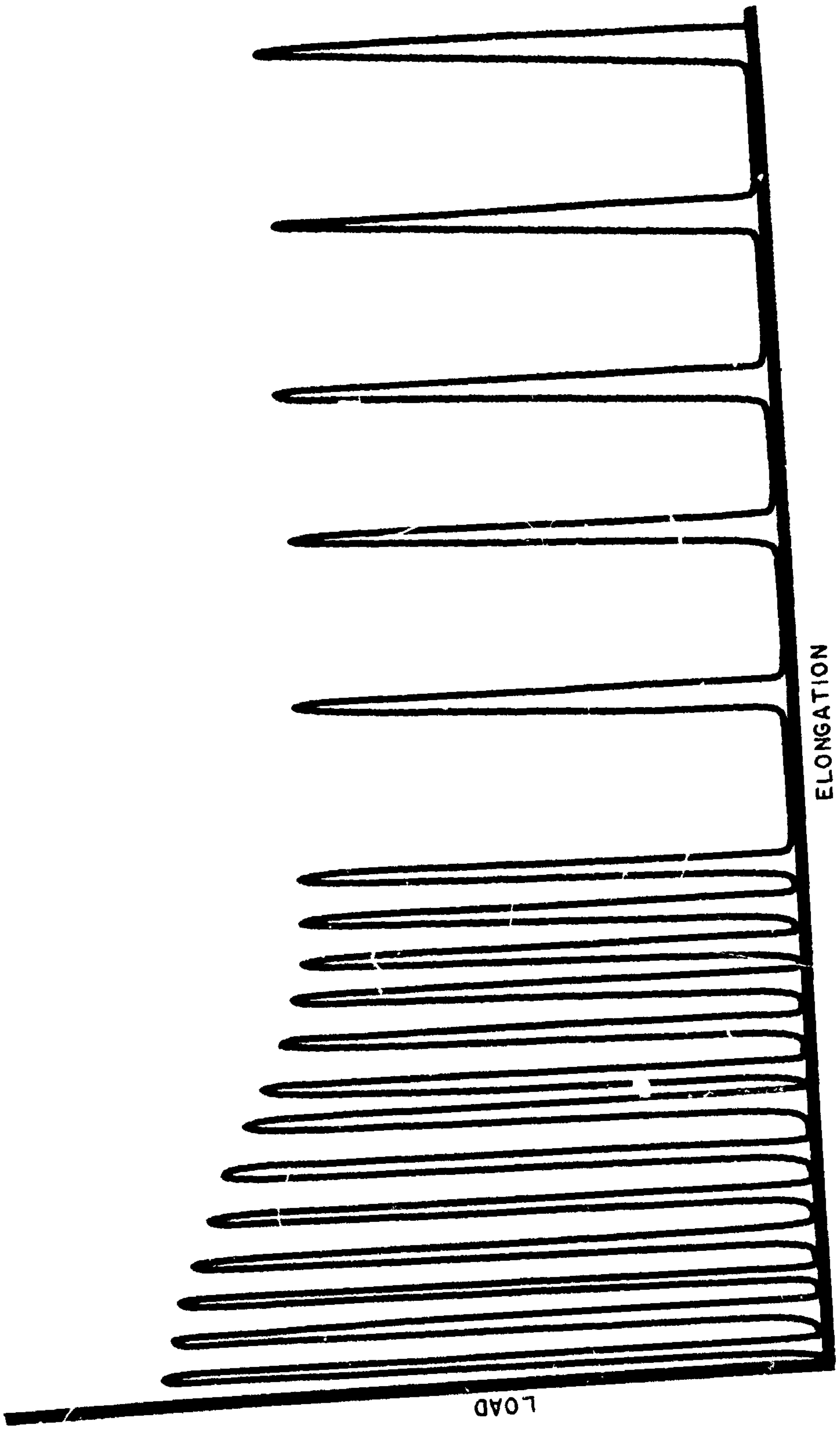

Fig 9 Sample completely unloaded at high point of yield peak

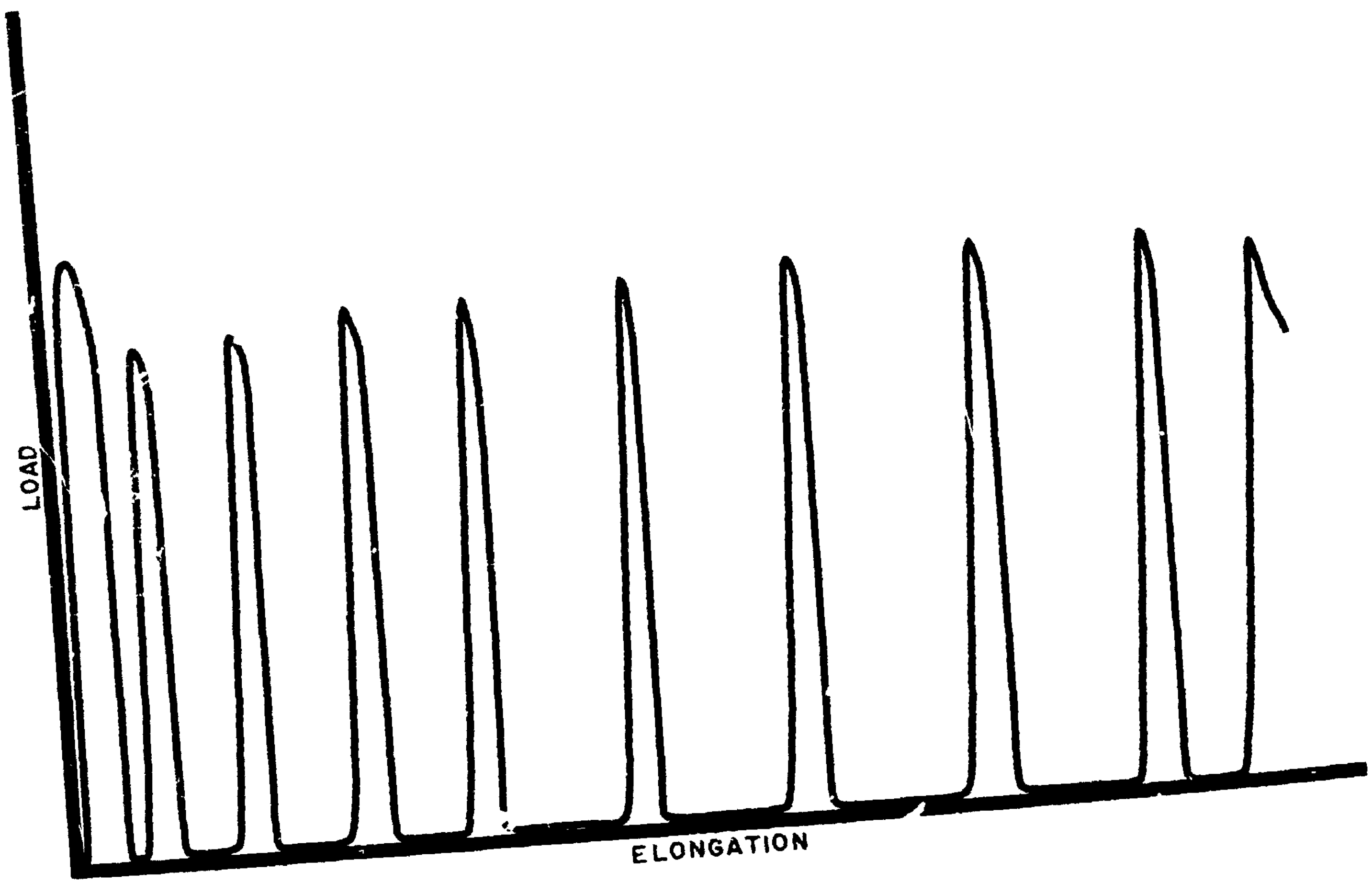

Fig 10 Sample completely unloaded after formation of yield peaks